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(54) Title: METHOD FOR THE PREPARATION OF A MEAT SUBSTITUTE PRODUCT, MEAT SUBSTITUTE PRODUCT OBTAINED WITH THE METHOD AND READY TO CONSUME MEAT SUBSTITUTE PRODUCT

(57) Abstract: The invention relates to a method for the preparation of a meat substitute product in which a protein, a hydrocolloid which precipitates with metal cations and water are mixed at elevated temperature until a homogenous mixture is formed. The mixture is mixed with a solution of a metal cation with a valency of at least 2 to form a fibrous product. The fibrous product is then obtained. The protein used is a material which comprises animal protein or a material derived therefrom, such as curd, cheese, powdered milk or the like. The hydrocolloid is selected from pectin with a low methoxyl group content, gellan gum and alginate. The invention also describes the meat substitute product which is obtained with the aid of the method according to the invention. Furthermore, the invention describes a ready to consume meat replacement product prepared by culinary processing of the meat substitute product which has been explained and has been obtained with the aid of the method according to the application.



Short title: Method for the preparation of a meat substitute product, meat substitute product obtained with the method and ready to consume meat substitute product

The invention relates to a method for the preparation of a meat substitute product which comprises protein, wherein:

- a protein material, a hydrocolloid which precipitates with
   metal cations and water are added to one another,
  - 2) the composition from step 1) is formed into a homogenous mixture,
- 3) the mixture from 2) is mixed with a solution of a metal cation with a valency of at least 2, in order to form a fibrous 15 product,
  - 4) the fibrous product is isolated.

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The fibrous product, possibly after further processing, forms a meat substitute product.

20 A method of this type is known from NL-C-1008364, in the name of A.C. Kweldam.

The said patent describes a method of the type described in the introduction for processing non-animal proteins, such as proteins derived from soya, rice, maize and the like, to form meat substitutes. It is assumed that the homogenous mixture as described above contains complexes of protein and hydrocolloid which precipitates with metal cations, which are precipitated in the form of fibres on account of the addition of a solution of a metal cation with a valency of at least 2.

The applicant has attempted to use the method described to convert milk protein or materials derived from milk protein into a fibrous meat substitute product.

In the method described, a homogenous mixture of protein, hydrocolloid which precipitates with metal cations and water is generally made by stirring at a temperature in the range from 20 to 90°C, more particularly from 30 to 90°C, and generally at

a temperature of approximately 50°C.

At a slightly elevated temperature, the protein will melt and form a homogenous mixture with the hydrocolloid which precipitates with metal cations and water.

It should be noted that the term homogenous mixture in the present application is used to cover both emulsions, dispersions and solutions.

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With some proteins, for example cheese milk protein, the use of an elevated temperature will lead to melting, with the result that the homogenous mixture is a distribution of two liquid materials which are not soluble in one another, i.e. an emulsion. With other milk proteins, there will be no melting, but rather dispersion or dissolution will take place.

In addition to the presence of organoleptic benefits, milk protein material is distinguished from vegetable protein through the absence of trypsin inhibitors (which are present in vegetable protein material, such as soya and maize) and a superior amino acid pattern. The PDCAAS (protein digestability corrected amino acid score) of protein from cow's milk is 1.21, while that of soya is 0.91 and that of wheat is 0.42. Normal beef has a score of 0.92; therefore, the milk protein material actually scores better than meat.

When the method described in the preamble is applied to milk protein or a material derived therefrom, the desired homogenous mixtures is not obtained or is difficult to obtain.

It is an object of the present invention to provide a solution to this drawback, and to this end the present invention is characterized in that the protein material comprises a milk protein material, and the mixture of protein material, hydrocolloid which precipitates with metal cations and water is formed in the presence of an amount of a phosphate material.

This is because one problem is that the free calcium ions which

are naturally present in milk protein or materials derived therefrom or are added during processing may form a precipitate with the added hydrocolloid, which precipitates with metal cations, prematurely, which has a highly adverse effect on the further sequence of the method and may lead to a serious lack of uniformity in the finished product, if a usable end product can be obtained at all.

In the method according to the invention described above, the presence of a suitable amount of phosphate material means that a complex is formed with the free Ca<sup>2+</sup> ion content, with the result that there is no premature precipitation of the hydrocolloid used. A homogenous mixture is then obtained without problems.

In addition to having the effect of forming a complex with free calcium ions, phosphate also has a protein-digesting action. The protein-digesting action manifests itself, inter alia, in an improved water uptake and has a positive effect on the sensation in the mouth.

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It is expedient firstly to make up a mixture of protein material and water and to add the phosphate material to this mixture. Then, the hydrocolloid which precipitates with metal cations with a valency of at least 2 is added, and the mixture is stirred until a homogenous mixture is obtained. In addition to stirring, it is also possible to use other distribution methods, such as homogenization, milling, dispersion and the like.

The method can be used, inter alia, with a number of milk protein materials which are isolated during cheesemaking, specifically cheese curd, cheese and cheese products; it is possible for materials such as powdered milk, sodium caseinate, calcium caseinate (generally alkali metal, akaline-earth metal and ammonium caseinate), whey protein, crosslinked caseine and the like to be processed.

Obviously, it is also possible to use mixtures of two or more protein materials to prepare a meat substitute product.

In a method which is directed at the processing of materials such as cheese curd and cheese, to prepare a meat substitute product the starting material is if desired converted into a finely distributed form (for example cheese is grated), and is mixed with water, hydrocolloid which precipitates with metal cations and phosphate material in an amount which is sufficient to form a complex with free calcium ions which are present. This is followed by extensive mixing to obtain a homogenous mixture.

The phosphate material makes it possible to form a homogenous mixture, such as an emulsion, from protein material, such as milk protein material, a hydrocolloid which precipitates with metal cations and water at elevated temperature.

The hydrocolloid which precipitates with metal cations, and is a polysaccharide, may be selected from pectin with a low methoxyl group content, Gellan gum and alginate; sodium alginate is preferred. There are numerous commercially available alginates; in the context of the invention, use is made of, for example, Ca-reactive alginates such as of the type obtained from "Brown algae".

If a solution of a metal cation with a valency of at least 2 is added to the homogenous mixture in which there are substantially no longer any free calcium ions and which contains complexes of milk protein material and a hydrocolloid which precipitates with metal cations of this type, a fibrous product will be obtained in a controlled way and, optionally after washing and removal of excess moisture, has a meat substitute structure.

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In connection with the invention, reference is also made to US-A 4,559,233.

The said patent describes the formation of a meat substitute starting from whey protein.

Whey protein/xanthan gum complexes, which are precipitated isoelectrically, are formed.

This publication does not describe the use of hydrocolloid which precipitates with metal cations, the formation of a complex between free calcium ions which are present and a phosphate material and the precipitation step using a solution of metal cations with a valency of at least 2.

In the present method, a solution of a metal cation with a valency  $\geq 2$  is added to the homogenous mixture, after it has been formed, in order to form milk protein/hydrocolloid fibres, such as milk protein/alginate fibres.

The metal cation solution generally contains soluble calcium or magnesium salts or mixtures thereof. Suitable calcium salts are calcium chloride, calcium acetate and calcium gluconate.

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The phosphate material which is to be used for milk protein material which contains free calcium ions is generally a phosphate material which is able to form a complex with metal cations with a valency of at least 2, such as calcium or magnesium, and is expediently selected from alkali metal and ammonium salts of phosphoric acid of polyphosphoric acid.

The phosphate material may, for example, be disodium hydrogen phosphate, trisodium phosphate or sodium hexametaphosphate.

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The phosphate material may also be sodium polyphosphate  $(NaPO_3)_n$  where  $n \sim 25$ .

The amount of phosphate material to be used is at least sufficient to form a complex with the free calcium ions which are present. In view of the protein-digesting action of phosphate as described above, in certain cases an excess of phosphate may be desirable and will even be generally applied.

35 The phosphate material is expediently added in an amount from 0.1 to 1.5% by weight, based on the total of all the constituents of the homogenous mixture.

The salts, phosphates and the like which are to be used will in

all cases be of a type and purity which are licensed for use in foodstuff.

With regard to the phosphate material which is used to form a 5 complex with the free calcium ions, it should also be noted that this is a readily available material which offers advantages in terms of its price. However, other complex-forming agents are not ruled out; for example, if desired a known complex-forming agent such as EDTA of food-grade quality can also be used with the same effect. Other similar agents can also successfully be used.

The hydrocolloid which is sensitive to metal cations may be selected from the group described above; however, it is expedient for the hydrocolloid to be sodium alginate.

Examples of suitable alginates are DMB sodium alginate (Manugel) from Kelco and FD125 from Danisco Cultor. It is also possible to use other alginates which form a precipitate with metal cations.

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During the formation of the meat substitute products according to the present invention, the pH of the homogenous mixture of protein, hydrocolloid which precipitates with metal cations and water is advantageously set to a value in the range from 4 to 7.

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Where the pH lies within this range will be selected according to the structure type of the meat substitute material which it is desired to prepare.

30 For example, to prepare a meat-type structure starting from a milk protein material, the pH will be set to a value between 5.0 and 7.0.

In the context of the present invention, the term meat-type structure is understood as meaning a structure which corresponds 35 to the structure of beef, pork or chicken.

If a fish-type structure is desired, starting from milk protein material, the pH is set to a value between 4.5 and 6.0.

Specific details of the meat- or fish-type structure can be produced by varying the quantity of hydrocolloid, such as sodium alginate, used and also the type of alginate and the amount of calcium chloride.

In general, it is also possible to add finishing materials; they are preferably added to the homogenous mixture of protein, hydrocolloid which precipitates with metal cations and water, which is formed at elevated temperature. The finishing material may be selected from a flavouring, a colouring, vegetable or animal fat, vegetable or animal proteins and/or mixtures of two or more of these materials. Obviously, it is also possible for finishing materials to be added and mixed in after the fibrous product has been formed.

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In a number of specific embodiments in which different starting materials are used, the method as described takes the following form.

- 20 Firstly, to form a fibrous product starting from cheese curd;
  - identical quantities by weight of cheese curd and water at approximately 50°C are mixed (total weight 2A) in the presence of 0.8 1.2% by weight, based on 2A, of sodium polyphosphate,
- 2.5 3.5% by weight, based on 2A, of sodium alginate, as well
   as water at approximately 50°C in an amount by weight A, are added with stirring,
  - the homogenous mixture formed is mixed with stirring with a 3
     5% by weight strength CaCl<sub>2</sub> solution in an amount by weight A to form a fibrous product,
- 30 after which the fibrous product formed is isolated and finished.

In another embodiment, to form a fibrous product starting from cheese:

- identical quantities by weight of grated cheese and water at approximately 50°C are mixed (total weight of 2B) in the presence of 0.8 1.2% by weight, based on 2B, of sodium polyphosphate,
  - 2.5 3.5% by weight, based on 2B, of sodium alginate, as well

as water at approximately 50°C in an amount by weight B, are added with stirring,

- the homogenous mixture formed is mixed with stirring with a 3-5% by weight strength  $CaCl_2$  solution in an amount by weight B to form a fibrous product,
- after which the fibrous product formed is isolated and finished.

In yet another embodiment, the formation of a fibrous product starting from sodium caseinate is characterized in that

- a 10 15% strength by weight solution of sodium caseinate in water is made (total weight C) in the presence of 0.2 0.4% by weight of sodium polyphosphate, based on C
- butter is added in an amount of 15 20% by weight, based on
   C,
  - 3 5% by weight, based on C, of sodium alginate, as well as water at approximately  $50^{\circ}$ C in an amount by weight of 80 95% by weight, based on C are added with stirring,
- the homogenous mixture formed is mixed with stirring with
   3 5% strength by weight calcium chloride solution in an amount of 80 95% by weight, based on C, to form a fibrous product, and
  - · the fibrous product formed is isolated and finished.

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- 25 In yet another embodiment, the method according to the invention is characterized in that, to form a fibrous product starting from whey protein
  - a 15 20% strength by weight solution of whey protein in water is made (total weight D) in the presence of 0.2 0.4% by weight of sodium polyphosphate, based on D,
  - butter is added in an amount of 12 18% by weight, based on D,
  - 3 7% by weight, based on D, of sodium alginate, as well as water at approximately  $50^{\circ}$ C in an amount of 80 85% by weight, based on D, are added with stirring, and
  - the homogenous mixture formed is mixed with stirring with 3-5% strength by weight calcium chloride solution in an amount of 80-85% by weight, based on D to form a fibrous product,
  - · the fibrous product formed is isolated and finished.

According to the invention, to form a fibrous product starting from skimmed milk powder,

- a 25 35% strength by weight solution of skimmed milk powder in water (total weight E) is made in the presence of 0.5 - 1.0% by weight, based on E, of sodium polyphosphate,
  - butter is added in an amount of 11 15% by weight, based on
     E,
- 4 6% by weight, based on E, of sodium alginate, as well as
   water at approximately 50% C in an amount by weight of 65 75%, based on E, are added with stirring,
  - the homogenous mixture formed is mixed with stirring with a 3-5% strength by weight  $CaCl_2$  solution in an amount by weight of 65-75%, based on E, to form a fibrous product,
- 15 after which the fibrous product formed is isolated and finished.

In the specific embodiments given above, the quantities by weight and percentages are given as accurate numbers; however, it should be understood that deviations from these accurate values are permitted and that the values are intended to give an indication of the order of magnitude (by weight) of the materials with respect to one another.

- As has been discussed above, when the method is carried out with a view to converting a milk protein material into a fibrous meat substitute product, without the presence of phosphate material, the homogenous mixture which is to be formed will not be formed or will only be formed with difficulty, since the calcium ions which are naturally present or are added during processing lead to premature precipitation of the hydrocolloid or polysaccharide used, resulting in a product with less cohesion which is more difficult to cut.
- 35 Surprisingly, it has now been found that the present method, for certain milk protein materials, can even be carried out without the presence of phosphate material, and a homogenous mixture can be formed and a good fibrous product obtained without problems.

In a particular embodiment, therefore, in the method described above the protein material comprises a milk protein material selected from powdered milk, whey protein and caseinate (in particular food-grade alkali metal or ammonium caseinate), and the method is carried out in the absence of a phosphate material.

This is because it has been found that the abovementioned materials contain either little calcium per se (such as alkali netal or ammonium caseinate, in particular sodium caseinate, and whey protein) or relatively small amounts of free calcium ions (such as powdered milk), and that in such a case good results are obtained even if the phosphate is omitted. One possible explanation for this is that materials of this type undergo a preparation process in which the calcium which is present is substantially removed (alkali metal or ammonium caseinate and whey protein) and/or the calcium is bonded in some way (powdered milk).

- 20 Since this subject also has independent inventive value, the method which can be used for this selection of materials is repeated below in the form of an independent claim.

  Method for the preparation of a meat substitute product which comprises protein, wherein:
- 25 1) a protein material, a hydrocolloid which precipitates with metal cations and water are added to one another,
  - 2) the composition from step 1) is formed into a homogenous mixture,
- 3) the mixture from 2) is mixed with a solution of a metal 30 cation with a valency of at least 2, in order to form a fibrous product,
  - 4) fibrous product is isolated, characterized in that
- 5) the protein material comprises a milk protein material selected from the group consisting of powdered milk, whey protein and caseinate.

The latter-mentioned caseinate is expediently alkali metal or ammonium caseinate of food-grade quality.

The abovementioned series of milk protein materials forms,

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within the range of these materials, a selection which successfully leads to a product which can be used with success without phosphate. The digesting action of the phosphate discussed above is absent in these cases; nevertheless, the product obtained is readily suitable for consumption.

The particular embodiments which are described in the dependent claims of the present application, where they do not relate to the use of a phosphate material, are also of value in the "phosphate-free" method described above, i.e. the subject matter of claims 9 - 14, 21 - 22 is also deemed to be incorporated in the independently formulated method described above, in the form of particular embodiments.

The fibrous product which is obtained with the aid of the method according to the invention is expediently packaged after it has been shaped, isolated and finished as appropriate. A suitable packaging method is a vacuum-packaging method in which the product is placed into plastic packaging, for example made from polyethylene, under a vacuum and the packaging is sealed. Other packaging methods which can be used in this field may also be employed.

Before or after it has been packaged, the fibrous product may be subjected to a preserving treatment, such as pasteurization or steralization. Pasterurization will in many cases be sufficient (for example at 62.8 - 65.5°C for 30 min). In addition to pasteurization, it is also possible to use other preservation techniques, such as the addition of preservatives or stabilizers (Na ascorbate, benzoic acid), pH adjustment, etc.

The invention also relates to a meat substitute product which is obtained with the aid of the method described above.

substitute product which is obtained by culinary processing of the meat substitute product obtained according to the invention.

The product which is obtained with the aid of the method can be

cooked in the oven, grilled, poached, smoked and the like without problems; it can also be converted into snacks, sausages or the like. With regard to snacks, it should be noted that they may be savoury, for which purpose the flavourings required can be used. However, in view of the dairy nature of the starting materials, the fibrous product which is obtained using the method according to the invention is also eminently suitable for forming a sweet dessert-type product.

- The fibrous product is a meat or fish substitute product or a savoury or sweet dessert-like snack, in which the fibres formed adhere to one another naturally. The appearance of the products obtained is of a culinary nature, the colour is white and the fibres have an appearance similar to that of meat fibres. After processing by baking, braising, smoking, microwave heating or other treatment, it has a true meat or fish appearance and sensation in the mouth or a fibrous dessert sensation if a material which has been/can be made sweet is used.
- The homogenous mixture which is formed in the method generally contains 0.1 to 50% by weight of protein material, such as milk protein or products derived therefrom, preferably 1 to 40% by weight, based on dry matter.
- The hydrocolloid which precipitates with metal cations, such as for example sodium alginate, is present in an amount of from 0.1 to 10% by weight, in particular 1 to 5% by weight; the phosphate or polyphosphate is present in an amount of from 0.1 to 1.5% by weight, all percentages relating to the total weight of the homogenous mixture which is prepared in order to form the fibrous meat substitute product.

The solution used to form fibres, which is a solution of a metal cation with a valency of at least 2 as described above, generally has a concentration of from 0.01 to 15% by weight, preferably 0.05 to 10% by weight.

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The strength of the fibre, which is related to the sensation in the mouth when a bite is taken, is affected by the salt

concentration. For example, a higher salt concentration results in a stronger fibre.

After the formation of the homogenous mixture, which takes place at a temperature of 20 to 90°C, in particular 30 to 90°C and more particularly 50°C, the homogenous mixture is held at this temperature and the solution of a metal cation with a valency of at least 2, for example a calcium chloride solution, is added at approximately the same temperature.

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The salt solution is added with stirring, generally gradually.

The salt solution for the precipitation of the fibres will generally contain 0.01 to 15% by weight of salt, for example CaCl<sub>2</sub> or Ca acetate. The CaCl<sub>2</sub> concentration is advantageously selected to lie in the range between 0.5 and 8% by weight; it is preferable for the concentration to be no higher than 4% by weight.

20 The total amount of salt solution will typically be added over the course of 0.5 to 5 minutes, in particular 1 minute for a batch size of 1 kg.

The addition is expediently effected by spraying a salt solution onto the homogenous mixture which is at a relatively high temperature; the salt solution will preferably be at a temperature which corresponds to the temperature of the homogenous mixture.

The homogenous mixture may contain fat, such as milk fat originating from the milk from which the protein was separated. In this case, the fat content may be between 1 and 6% by weight, more particularly between 2.5 and 5% by weight, based on the total weight of the homogenous mixture.

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Obviously, if a protein product in which there is no fat (anymore) is used, fat can be added to the homogenous mixture. In this case, it is possible to choose from vegetable and animal fats; it will be expedient to use a saturated or unsaturated

vegetable fat. Mixtures of fats can also be used.

Furthermore, colourings and flavourings can be added to the homogenous mixture.

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After the fibrous product has been formed, it is thoroughly washed in order to remove residues of metal cations, and the excess moisture is also removed, for example by pressing. The finished product may, for example, be vacuum-packed, after which pasteurization takes place in order to further consolidate the product and also to obtain a good shelf life. Vacuum-packing has the further advantage that the structure of the product is improved further through compression of the fibres.

After washing and pressing, the fibrous product obtained has a residual moisture content of from 1 to 80% by weight, in particular 40 to 60% by weight. However, levels which are higher and lower than these particular levels are possible, depending on what is desired.

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The invention will now be explained with reference to a number of non-limiting examples.

In the experiments, sodium alginate (Kelco DMB) was used as 25 hydrocolloid which precipitates with metal cations; the precipitation solution used contained 4% by weight of CaCl<sub>2</sub> in water.

The phosphate material used was sodium polyphosphate  $(NaPO_3)_n$  where n ~ 25. All the percentages are based on weight, unless otherwise indicated.

### Example I: Cheese curd as starting material

A mixture of 600 grams of curd (Maasdam curd (45+ % fat in dry matter), calcium content: 533 mg/100 g, moisture content 63.4%) and 600 ml of water with a temperature of 55°C and 12 grams of sodium polyphosphate (NaPO<sub>3</sub>)<sub>n</sub> where n ~ 25 is prepared. The mixture is transferred to a high-speed mixer. 40 Grams of sodium

alginate (Kelco, Manugel DMB) and 600 ml of water are added with continuous mixing. The mixture prepared is sprayed with 600 ml of a 4% strength by weight calcium chloride (CaCl<sub>2</sub>) solution with continuous stirring. The ratio between cheese curd weight and the total weight of water is in this case 1 to approximately 3. During stirring, a fibre is formed and is removed from the residual liquid. After washing and pressing into the desired shape, a meat substitute with a structure resembling chicken and good cohesion is obtained. After pasteurization of the end product, the abovementioned method results in a product with a long shelf life.

### Example II: Cheese as starting material

An amount of 600 grams (50+ % fat in dry matter) of cheese of 15 the Maasdam type which has been ripened for 5 weeks (calcium content: 786 mg/100 grams, moisture content 39.5%) in grated form is mixed with 12 grams of sodium polyphosphate and 600 ml of water at approximately 55°C. 40 Grams of sodium alginate (Kelco DMB) and 600 ml of water at 55°C are added to this more 20 or less homogenous mass in a high-speed mixer with continuous mixing. The thick mass formed is gradually mixed with 600 ml of a 4% strength by weight calcium chloride solution until fibre formation is complete. The fibres formed are removed and are 25 washed in ample water in order to remove the excess calcium chloride. The fibrous mass is pressed into the desired shape, packaged and pasteurized. The meat substitute obtained in this way has a moisture content of 58 to 68%, a pleasant cheesy taste and a short fibre structure.

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### Example III: Sodium caseinate as starting material

The method started from 85 grams of sodium caseinate (DMV International, sodium caseinate) with a calcium content of 76 mg/100 grams, a protein content of 90% and moisture content of 5%. The sodium caseinate was dissolved in 600 ml of water at 45°C. 2 grams of sodium polyphosphate were added, followed by 110 grams of butter. After mixing to form a homogenous mixture, 30 grams of sodium alginate and 600 ml of warm water were added

with intensive mixing. The mixture obtained was treated with 600 ml of a 4% strength by weight calcium chloride solution until a long, strong fibre is obtained. After washing, pressing, flavouring and pasteurizing, this meat substitute product with a chicken structure and chicken flavour had a water content of 68 - 78%.

The advantage of using sodium caseinate is that there is no need for there to be whey-processing facilities onsite.

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## Example IV: Whey-protein concentrate as starting material

125 grams of whey-protein concentrate (Arla, Lacprodan 80, calcium content: 374 mg/100 grams, moisture content 5.5%) with a protein content of 82% is dissolved in 600 grams of water at 45°C and mixed with 2 grams of sodium polyphosphate and 110 grams of butter. After pressing/mixing, 40 grams of sodium alginate and 600 ml of water at 45°C are added to the mixture with intensive stirring. The mixture obtained is combined with 600 ml of a 4% strength by weight calcium chloride solution. 20 After washing and pressing, the meat product obtained is flavoured. After the product has been vacuum-packed and pasteurized, the result is a meat substitute with good cooking properties and a chicken-meat structure. The end product has a moisture content of 70 - 75%. 25

In a separate test, the abovementioned whey-protein concentrate was dissolved in water and then subjected to a denaturation treatment by heating for 10 minutes at 95°C. This was followed by cooling to 45°C and then the test was continued as described above. The result of the test was similar to the result of the original test described above; in this way, it was possible to limit the protein losses via the washing water.

### 35 Examp V: Powdered milk as starting material

The milk protein used is skimmed milk powder (calcium content: 1160 mg/100 grams, moisture content: 4%, protein content: 30%). An amount of 250 grams was dissolved in 600 ml of water to which

4 grams of sodium polyphosphate and 110 grams of butter were added. Then, 40 grams of sodium alginate and 600 ml of water were added to this mass. After treatment of the emulsion obtained with 600 ml of a 4% calcium chloride solution, a pleasant white fibre is obtained. Washing, pressing, flavouring, packaging and pasteurization results in a pleasant product with properties similar to those of meat. Without flavouring, the product has a neutral flavour similar to that of milk.

The above formulation which is based on powdered milk uses 4 grams of sodium polyphosphate. However, if the amount of calcium which is present is taken into consideration, it has been found that this amount can be increased to 8 grams, since, as with the other raw materials, there is an excess of phosphate material in the mixture.

Table 1 shows an overview of the tests carried out as well as the most important parameters.

In the examples discussed above, in the case of powdered milk, whey protein and sodium caseinate, it is possible to dispense with the use of a phosphate material yet still obtain an acceptable product, although the products which are prepared with phosphate material achieve slightly better scores in quality assessments.

In the case of powdered milk, it is generally also possible, by high pasteurization of the powdered milk solution, to obtain a good product with the advantage of lower protein losses in the washing water.

Table 1: Summary of tests carried out

erial	Raw Algi- material nate (g)	Phos- phate (g)	phos- phate (mmol)	Calcium in the raw material (mmol)	Net weight (g)	Weight of end pro- duct (g)	Produc	Product Composition	ositio	덕) 다		,  ()	د ر	بر د	Cal- cium IN (g)	Cal- cium OUT (g)	Δ Cal- cium (g)
								cium (mg/ 1009)	<del>}</del> €	(*)		fors- ture (%)	ASn (*)	on dry			
Maasdam curd (45+)	40	12	117.6	79.8	1103	619	5,45	1010	0.2	11.2	38.6	71.0	3.2	11.0	3.2	7.0	ສ. ສ
50+ cheese, Maasdam type	0 7	12	117.6	117.2	1274	751	5.52	1020	e. 0	22.0	50.8	56.7	ພ ນ	8.1	4.7	7.7	9°0
Sodium casei- nate	30	8	19.6	1.50	766 7	613	6.13	634	0.2	13.1	44.6	70.6	2.0	8.0	90.0	a. 0	3.8
	40	8	19.6	11.7	1027	645	5.83	268	0.2	13.2	52.2	74.7	1.9	7.5	0.47	3.7	3.2
Powdered m11k	40	4	39.2	72.3	 88	561	5.58	1060	0.5	13.5	38.4	64.8	3,3	4.0	2.9	5.9	3.1

Calcium In and Out is understood as meaning the quantity of calcium in the raw material (In) and in the end The 600 ml of CaCl<sub>2</sub> added contained approximately 8.7 grams of Ca<sup>2+</sup>. The final column of the table shows how product (Out).

many grams of calcium of these 8.7 grams were taken up by the fibre (out - in).

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#### CLAIMS

1. Method for the preparation of a meat substitute product which comprises protein, wherein:

- 1) a protein material, a hydrocolloid which precipitates with metal cations and water are added to one another,
- 2) the composition from step 1) is formed into a homogenous mixture,
- 10 3) the mixture from 2) is mixed with a solution of a metal cation with a valency of at least 2, in order to form a fibrous product,
  - 4) the fibrous product is isolated, characterized in that
- 15 5) the protein material comprises a milk protein material, and
  - 6) the mixture of milk protein material, hydrocolloid which precipitates with metal cations and water is formed in the presence of an amount of a phosphate material.
- 20 2. Method according to claim 1, characterized in that first of all a mixture of the protein material and water is made, the phosphate material is added to this mixture and then the hydrocolloid which precipitates with metal cations is introduced.

- 3. Method according to claim 1 or 2, characterized in that the milk protein material is selected from
- curd from cheesemaking
- cheese
- 30 powdered milk
  - whey protein
  - alkali metal, alkaline-earth metal and ammonium caseinate.
- 4. Method according to one or more of claims 1 3, 35 characterized in that the phosphate material is selected from alkali metal and ammonium salts of phosphoric acid or polyphosphoric acid.
  - 5. Method according to claim 4, characterized in that the

phosphate material is selected from disodium hydrogen phosphate, sodium hexametaphosphate and trisodium phosphate.

- 6. Method according to claim 4, characterized in that the phosphate material is sodium polyphosphate  $(NaPO_3)_n$ , where  $n \sim 25$ .
- 7. Method according to one or more of claims 1 6, characterized in that the amount of phosphate material is at 10 least sufficient to form a complex with free calcium ions which are present.
- Method according to claim 7, characterized in that the amount of phosphate material is 0.1 1.5% by weight, based on the total of all the constituents of the homogenous mixture.
  - 9. Method according to one or more of the preceding claims, characterized in that the hydrocolloid which precipitates with metal cations is present in an amount of 0.1 10% by weight, based on the total of all the constituents of the homogenous mixture.
- 10. Method according to claim 9, characterized in that the hydrocolloid which precipitates with metal cations is sodium 25 alginate.

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- 11. Method according to one or more of the preceding claims, characterized in that the pH of the homogenous mixture of protein, hydrocolloid which precipitates with metal cations, phosphate material and water is set to a value in the range from 4-7.
- 12. Method according to claim 11, characterized in that to prepare a product with a meat-type structure starting from milk protein material, the pH is set to a value between 5.0 and 7.0.
  - 13. Method according to claim 11, characterized in that to prepare a product with a fish-type structure starting from milk protein material, the pH is set to a value between 4.5 and 6.0.

14. Method according to one or more of the preceding claims, characterized in that a finishing material selected from flavouring, colouring and vegetable or animal fat, vegetable or animal protein and/or mixtures of two or more such materials is added to the homogenous mixture which has been formed.

- 15. Method according to one or more of claims 1 -14, characterized in that
- 10 to form a fibrous product starting from cheese curd:

- identical quantities by weight of cheese curd and water at approximately 50°C are mixed (total weight 2A) in the presence of 0.8 1.2% by weight, based on 2A, of sodium polyphosphate,
- 2.5 3.5% by weight, based on 2A, of sodium alginate, as well as water at approximately 50°C in an amount by weight A, are added with stirring,
  - the homogenous mixture formed is mixed with stirring with a 3-5% by weight strength  $CaCl_2$  solution in an amount by weight A to form a fibrous product,
- 20 the fibrous product formed is isolated and finished.
  - 16. Method according to one or more of claims 1 14, characterized in that
  - to form a fibrous product starting from cheese:
- identical quantities by weight of grated cheese and water at approximately 50°C are mixed (total weight of 2B) in the presence of 0.8 1.2% by weight, based on 2B, of sodium polyphosphate,
  - 2.5 3.5% by weight, based on 2B, of sodium alginate, as well
     as water at approximately 50°C in an amount by weight B, are added with stirring,
    - the homogenous mixture formed is mixed with stirring with a 3-5% by weight strength  $CaCl_2$  solution in an amount by weight B to form a fibrous product,
- the fibrous product formed is isolated and finished.
  - 17. Method according to one or more of claims 1 14, characterized in that
  - to form a fibrous product starting from sodium caseinate:

• a 10 - 15% strength by weight solution of sodium caseinate in water at approximately  $50^{\circ}$ C is made (total weight C) in the presence of 0.2 - 0.4% by weight of sodium polyphosphate, based on C,

- butter is added in an amount of 15 20% by weight, based on C,
  - 3 5% by weight, based on C, of sodium alginate, as well as water at approximately  $50^{\circ}$ C in an amount by weight of 80 95% by weight, based on C are added with stirring,
- the homogenous mixture formed is mixed with stirring with
  5% strength by weight calcium chloride solution in an amount of 80 -95% by weight, based on C, to form a fibrous product, and
  the fibrous product formed is isolated and finished.
- 15 18. Method according to one or more of the preceding claims  $1\,-\,14$ , characterized in that

to form a fibrous product starting from whey protein,

- a 15 20% strength by weight solution of whey protein in water at approximately 50 °C is made (total weight D) in the
- 20 presence of 0.2 0.4% by weight of sodium polyphosphate, based on D,
  - butter is added in an amount of 12 18% by weight, based on  $D_{\star}$
- 3 7% by weight, based on D, of sodium alginate, as well as
   25 water at approximately 50°C in an amount of 80 85% by weight,
   based on D, are added with stirring, and
  - the homogenous mixture formed is mixed with stirring with 3-5% strength by weight calcium chloride solution in an amount of 80-85% by weight, based on D to form a fibrous product,
- 30 the fibrous product formed is isolated and finished.
  - 19. Method according to one or more of the claims 1 14, characterized in that
  - to form a fibrous product starting from powdered milk:
- a 25 35% strength by weight solution of skimmed milk powder in water (total weight E) is made in the presence of 0.5 1.0% by weight, based on E, of sodium polyphosphate,
  - butter is added in an amount of 11 15% by weight, based on E,

• 4 - 6% by weight, based on E, of sodium alginate, as well as water at approximately 50% C in an amount by weight of 65 - 75%, based on E, are added with stirring,

- the homogenous mixture formed is mixed with stirring with a
- 3 5% strength by weight CaCl<sub>2</sub> solution in an amount by weight of 65 75%, based on E, to form a fibrous product,
  - the fibrous product formed is isolated and finished.
- 20. Method according to one or more of claims 1 14, 10 characterized in that the protein material is milk protein material selected from powdered milk, whey protein and caseinate, and the method is carried out in the absence of a phosphate material.
- 15 21. Method according to one or more of claims 1 20, characterized in that the fibrous product, after it has been formed and isolated, is pasteurized in order to be finished.
- 22. Method according to one or more of claims 1 21, 20 characterized in that the fibrous product is packaged.
  - 23. Meat substitute product obtained using the method according to one or more of claims 1 21.
- 25 24. Savoury or sweet snack obtained by processing a fibrous product formed with the aid of the method according to one or more of claims 1 21.
- 25. Ready to consume meat substitute product obtained by culinary processing of a product according to claim 23.

#### INTERNATIONAL SEARCH REPORT

PCT/NE 02/00594

A. CLASSIFICATION OF SUBJECT MATTER
1PC 7 A23J3/08 A23J3/10 A23J3/22 A23L1/0524 A23L1/0532 A23L1/054 A23L1/059 According to International Patent Classification (IPC) or to both national classification and IPC B. FIELDS SEARCHED Minimum documentation searched (dassification system followed by classification symbols) A23J A23C A23L Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data, PAJ, FSTA, BIOSIS C. DOCUMENTS CONSIDERED TO BE RELEVANT Category \* Citation of document, with indication, where appropriate, of the relevant passages Relevant to dalm No. US 3 093 483 A (ERIC ENGEL ET AL) X 1-25 11 June 1963 (1963-06-11) column 3, line 65 -column 4, line 48; claims 20,21; example 4 X NL 1 008 364 C (KWELDAM A C K) 1-25 1 November 1999 (1999-11-01) cited in the application page 1, line 23-32; claims 1,2,4,10 page 2, line 25 -page 3, line 7; example 1 χ US 3 627 536 A (HARADA YOICHI ET AL) 1-25 14 December 1971 (1971-12-14) column 1, line 49 -column 2, line 41; claim 5; example 2 -/--Further documents are listed in the continuation of box C. Patent family members are listed in annex. Special categories of cited documents: \*T\* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance Invention "E" earlier document but published on or after the International "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu-"O" document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled in the art. \*P\* document published prior to the international filling date but later than the priority date claimed "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the International search report 27 January 2003 03/02/2003 Name and mailing address of the ISA Authorized officer European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Heirbaut, M Fax: (+31-70) 340-3016

# INTERNATIONAL SEARCH REPORT

PC1/NE 02/00594

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	otion) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category ®	Citation of document, with Indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 118 520 A (VISSER JOHANNES ET AL) 3 October 1978 (1978-10-03) column 2, line 1-28; claim 1; examples 1-4	1-25
X	WO 96 13177 A (MONSANTO CO) 9 May 1996 (1996-05-09) page 2, line 31 -page 3, line 4; claims 3,4,8 page 5, line 3 -page 6, line 6 page 6, line 29-34; examples 5-15	1-25
X	US 3 865 959 A (LECLUSE WILLEM JAN) 11 February 1975 (1975-02-11) column 2, line 57-66; claims 5,9; examples 2,3,5	1-25
X	US 4 423 083 A (SHENOUDA SOLIMAN Y K) 27 December 1983 (1983-12-27) column 2, line 50-68; claims 7-9 column 3, line 21-28 column 7, line 1-24 column 8, line 38 -column 9, line 7; examples 5,7-10	1-25
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# INTERNATIONAL SEARCH REPORT

PCT/NE 02/00594

					FCI/NL	02/00594
	atent document d in search report		Publication date		Patent family member(s)	Publication date
US	3093483	A	11-06-1963	NONE		
NL	1008364	С	30-08-1999	NL	1008364 C2	30-08-1999
US	3627536	Α	14-12-1971	NONE		هر دهاد آن چینی که بینگ که دها کا
US	4118520	A	03-10-1978	GB	1572395 A	30-07-1980
				BE	852911 A1	26-09-1977
				CA	1090075 A1	25-11-1980
				DE	2713375 A1	13-10-1977
				DK	122577 A	27-09-1977
				FR	2345086 A1	21-10-1977
				ΙE	44898 B1	05-05-1982
				IT	1082479 B	21-05-1985
				JP	1440222 C	30-05-1988
				JP	52118033 A	04-10-1977
				JP	62050095 B	22-10-1987
				LU	77023 A1	03-10-1977
		•		NL	7703073 A ,B,	28-09-1977
				SE	456474 B	10-10-1988
				SE	7703473 A	27-09-1977
				US	4208436 A	17-06-1980
WO	9613177	Α	09-05-1996	AU	4011095 A	23-05-1996
		,		WO	9613177 A1	09-05-1996
บร	3865959	Α	11-02-1975	NL	7116966 A	13-06-1973
				AR	206587 A1	06-08-1976
				AU	464293 B2	21-08-1975
				AU	4969772 A	06-06-1974
				BE	792473 A1	30-03-1973
				CA	994160 A1	03-08-1976
				DE	2260119 A1	20-06-1973
				FR	2162603 A1	20-07-1973
				GB	1398179 A	18-06-1975
				JP	877241 C	22-08-1977
				JP	48075754 A	12-10-1973
				JP	52002987 B	25-01-1977
US	4423083	Α	27-12-1983	CA	1160892 A1	24-01-1984
				EP	0037676 A2	14-10-1981
				JP	1056745 B	01-12-1989
				JP JP	1572813 C 56160947 A	20-08-1990 11-12-1981